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WPI Abstract Accession No. 1997-539607 [50] &
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(54) Abstract Title

Synergistic combination of aryl amine antioxidants in turbine oils

(57) The present invention relates to a turbine oil composition exhibiting enhanced antioxidantcy and thermal stability, and to a method for achieving that result in turbine oils. The gas turbine lubricating oil of the present invention comprises a major portion of an aliphatic ester base oil having lubrication properties and formed by the reaction of pentaerythritol and an organic monocarboxylic acid. The turbine oil further comprises arylamine antioxidants. Two commonly deployed arylamines are substituted diphenylamines (DPA) and phenyl-alpha-naphthylamine (PANA) that may also be substituted. This invention discloses a synergistic combination of an arylamine antioxidant formulation comprising a DPA, a PANA, and an oligomeric antioxidant formed by the reaction of DPAs and PANAs.

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SYNERGYSTIC COMBINATION OF ARYL AMINE ANTIOXIDANTS IN
AVIATION TURBINE OILS

This invention generally relates to ester-based, in particular diester and polyol ester-based, turbine oils, which exhibit superior antioxidancy and reduced deposit forming tendencies. More particularly, it is related to turbine oils comprising esters of pentaerythritol with fatty acids as base stocks further
5 comprising a synergistic combination of aryl amine antioxidants.

Organic compositions, such as mineral oils and lubricating compositions, are subject to deterioration by oxidation and in particular are subject to such deterioration at high temperatures in the presence of air. This deterioration often leads to buildup of insoluble deposits that can foul engine parts,
10 deteriorate performance, and increase maintenance. This is particularly the case for lubricating oils used in jet aircraft where wide temperature ranges and extreme operating conditions are likely to be encountered. Proper lubricating of aircraft gas turbines, for example, requires ability to function at bulk oil temperatures from as low as -55°C to as high as $230^{\circ} - 260^{\circ}\text{C}$.

15 Ester base lubricating oil compositions prepared from pentaerythritol and a mixture of fatty acids and containing selected additive combinations are well known. These lubricants are functional over a wide temperature range and exhibit good thermal and oxidative stability. The need for a still more effective, long lived ester base lubricant composition, however, is a major goal of
20 lubricant manufacturers. This invention addresses that continuing need.

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The present invention resides in a turbine oil composition exhibiting enhanced antioxidancy and resistance to deposit formation, and to a method for achieving that result in turbine oils.

5 The gas turbine lubricating oil of the present invention comprises a major proportion of synthetic polyol ester based base stock including diesters and polyol esters, preferably polyol ester based base stock and a minor proportion of a three component aryl amine antioxidant/deposit control additive. Specifically, the three components are (1) a substituted diphenyl amine (DPA), (2) a phenyl- α -naphthyl amine (PANA), and (3) an oligomer antioxidant made
10 by the reaction of a DPA and PANA. Other, conventional additives such as extreme pressure, pour point reduction, oxidative stability, anti-foaming, hydrolytic stability, improved viscosity index performance, anti-wear, and corrosion inhibitor additives and others may also be employed. Further, the three component aryl amine antioxidant package of this invention may also be
15 used together with other known antioxidant additives.

The synthetic polyol ester based base stock comprises the major portion of the fully formulated synthetic ester based lubricating oil composition. In general, the ester base fluid is present in concentrations from about 90 to 99 percent by weight of the composition.

20 It should be noted that the term "comprising" is used frequently throughout the description of this invention and also in the appended claims. "Comprising", as used in this application and the appended claims is defined as "specifying the presence of stated features, integers, steps, or components as recited, but not precluding the presence or addition of one or more other steps,
25 components, or groups thereof". Comprising is different from "consisting of", which does preclude the presence or addition of one or more other steps, components, or groups thereof.

The present invention provides a turbine oil having unexpectedly superior deposition performance comprising a major portion of a synthetic ester
30 base oil and minor portion of a three component aryl amine antioxidant additive. Synthetic esters include diesters and polyol esters. The three components

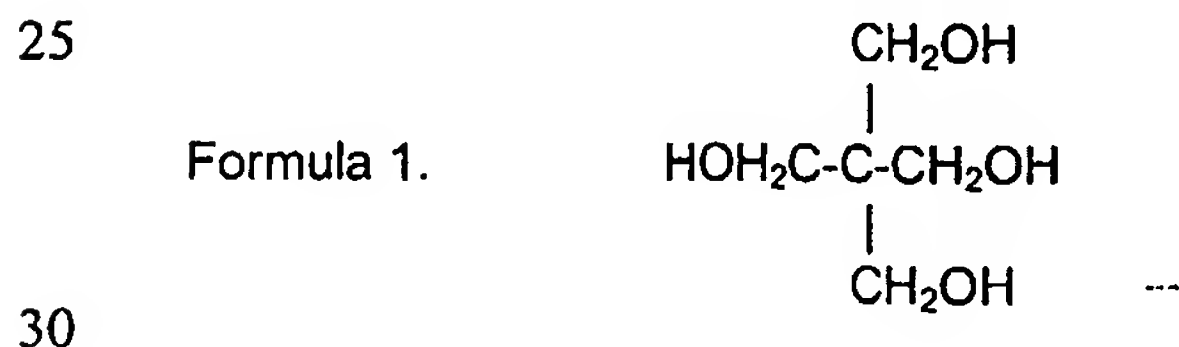
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antioxidant additives are (1) a substituted diphenyl amine (DPA), (2) a phenyl- α -naphthyl amine (PANA) which may be substituted or alkylated, and (3) an oligomer antioxidant made by the reaction of DPA's with PANA's.

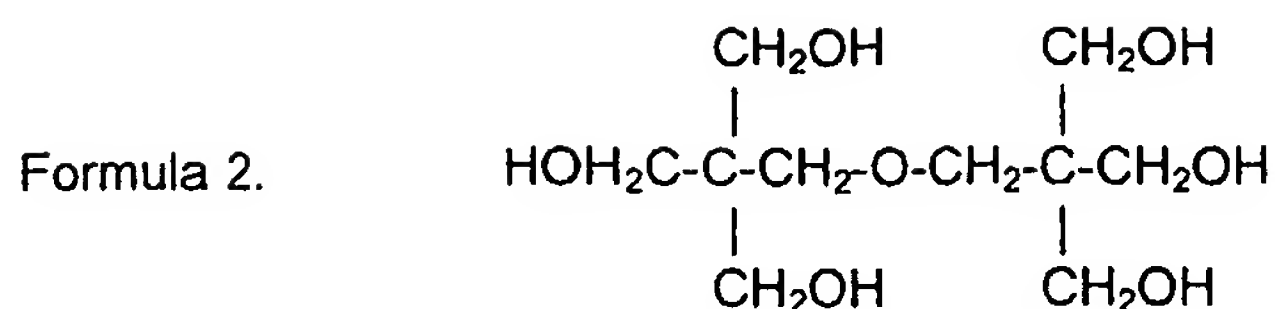
5 The diesters that can be used for the improved anti-deposition turbine oil of the present invention are formed by esterification of linear or branched C₆-C₁₅ aliphatic alcohols with one of such dibasic acids as adipic, sebacic, or azelaic acids. Examples of diesters are di-2-ethylhexyl sebacate and dioctyl adipate.

10 The synthetic polyol ester base oil is formed by the esterification of an aliphatic polyol with carboxylic acid. The aliphatic polyol contains from 4 to 15 carbon atoms and has from 2 to 8 esterifiable hydroxyl groups. Examples of polyol are trimethylolpropane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripentaerythritol and mixtures thereof.

15 The carboxylic acid reactant used to produce the synthetic polyol ester base oil is selected from aliphatic monocarboxylic acid or a mixture of aliphatic monocarboxylic acid and aliphatic dicarboxylic acid. The carboxylic acid contains from 4 to 12 carbon atoms and includes the straight and branched chain aliphatic acids. Mixtures of monocarboxylic acids may be used.

20 The preferred polyol ester base oil is one prepared from technical pentaerythritol and a mixture of C₄-C₁₂ carboxylic acids. Technical pentaerythritol is a mixture that includes about 85 to 92 wt % monopentaerythritol and 8 to 15 wt % dipentaerythritol. A typical commercial technical pentaerythritol contains about 88 wt % monopentaerythritol having Formula 1 and about 12 wt % of dipentaerythritol having Formula 2.





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The technical pentaerythritol may also contain some tri and tetra pentaerythritol which are typically formed as by-products during the production of technical pentaerythritol.

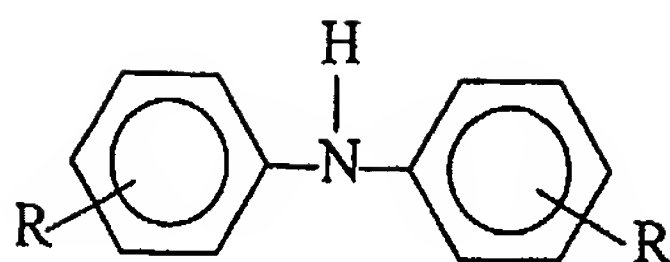
10 The preparation of esters from alcohols and carboxylic acids can be accomplished using conventional methods and techniques known and familiar to those skilled in the art, and form no part, per se, of the present invention. In general, technical pentaerythritol is heated with the desired carboxylic acid mixture, optionally in the presence of a catalyst. Generally, a slight excess of
15 acid is employed to force the reaction to completion. Water is removed during the reaction and any excess acid is then stripped from the reaction mixture. The esters of technical pentaerythritol may be used without further purification or may be further purified using conventional techniques such as distillation.

For the purposes of this specification and the appended claims, the term
20 "technical pentaerythritol ester" is understood as meaning the polyol ester base oil prepared from technical pentaerythritol and a mixture of C₄-C₁₂ carboxylic acids.

As previously stated, to the polyol ester base stock is added a minor portion of the three aryl amine antideposition and oxidation inhibition additive.
25 This three component additive will typically be used in an amount so as to comprise about 0.5 to about 10 wt % of the fully formulated lubricating oil composition. Each of the three essential components of the three component additive is described in detail below.

The diphenyl amine (DPA) component of the additive package is
30 represented by Formula 3.

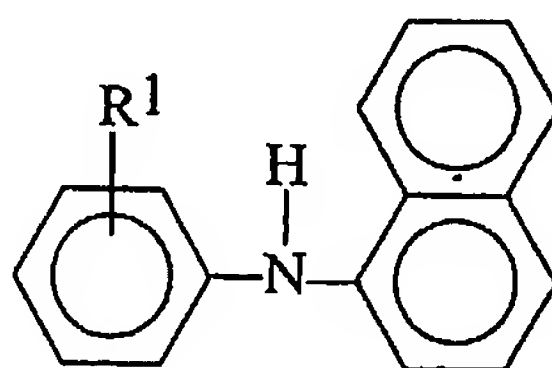
Formula 3



In Formula 3, R is an alkyl group having from about 4 to about 12 carbon atoms. Suitable alkylamines include dioctyldiphenylamine, didecyldiphenylamine, didodecyldiphenylamine, dihexyldiphenylamine and similar compounds. Dioctyldiphenylamine (DODPA) is the preferred compound and the preferred concentration is from about 0.2 to about 5.0 percent by weight of the fully formulated lubricating oil composition. These DPA compounds are commercially available.

10 The phenyl- α -naphthyl amine (PANA) component of the additive package is represented by Formula 4.

Formula 4

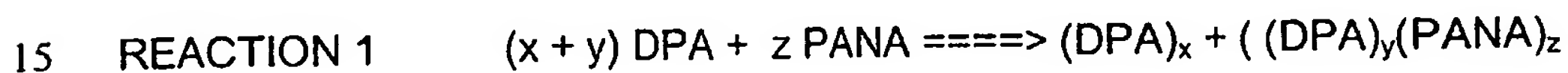


15 In Formula 4, R¹ may be H or an alkyl group containing from about 4 to 12 carbon atoms or an alkaryl group containing from 7 to 12 carbon atoms. The alkyl group can be straight or branched chain alkyl group with the tertiary alkyl structure being preferred or it can be an alkylaryl group.

20 Specific effective compounds of this class include phenyl alpha-naphthylamine, N-(para-tertiary-octylphenyl) alpha-naphthylamine, N-(4-cumylphenyl) alpha-naphthylamine and the corresponding parateritary-dodecylphenyl and parateritary-butylphenyl alpha-naphthylamines. The preferred naphthylamines are those in which R¹ is a tertiary alkyl group having from 6 to 10 carbon atoms therein. The preferred concentration of this

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component is from about 0.2 to about 5.0 percent by weight of the fully formulated lubricating oil composition. These PANA compounds are commercially available.

The third component of the three aryl amine antioxidant additive package is an oligomer formed by the reaction of a DPA component and a PANA component. More specifically the oligomer is produced by reacting a DPA with a PANA in the presence of one or more organic peroxides at an elevated temperature. The products of the reaction are a homo-oligomer of DPA and cross-oligomers of DPA and PANA. The DPA homo-oligomer formed covers a broad range of degree of oligomerization. Typically, under the conditions described above, about 75 weight percent of the oligomer consists of dimers, trimers, tetramers, and pentamers. Because DPA was defined by Formula 3 above and PANA was defined by Formula 4 above, the reaction can be simplified and generalized as shown by Reaction 1 below.



It is theorized that the bonding between the DPA and PANA may occur between two nitrogen atoms, between a nitrogen atom in one PANA or DPA and a carbon atom in another PANA or DPA, or between carbon atoms in two different aryl rings from naphthyl or phenyl groups. It is believed that most of the linkages between the DPA and PANA molecules are between a nitrogen in one DPA or PANA and a carbon atom in naphthyl or aryl substituents of another DPA or PANA. For those wanting a deeper understanding, the possible linkages are described in detail in U.S. Patent 3,509,214. Reaction 1 above is not meant only to imply that the cross-oligomers are block copolymers, however. The oligomers are believed to be very random in the order of DPA and PANA incorporation. The subscripts y and z are meant only to indicate the number of DPA or PANA molecules in the cross oligomer.

In order to get high conversion of the DPA and PANA to the desired oligomers, it is desirable that the DPA:PANA molar ratio be in the range of about 1:1 to 10:1; typically about 1.2:1 to about 5:1; more typically about 1.5:1

to about 4:1; preferably about 1.75:1 to about 2.5:1 or 3:1; and most preferably about 2:1.

The oligomization reaction may be conducted in bulk or solution by heating an admixture of DPA, PANA, and an organic peroxide to temperatures desirably in the range of about 70°C to 200°C for about 1 hour to 10 hours. The individual components can be added in any order, in increments, or metered into other components. The reaction may be carried out under vacuum to remove volatiles from the decomposition of the organic peroxides, if desired. The DPA and PANA may be dissolved in suitable organic solvents such as aliphatic hydrocarbons or synthetic ester lubricants, which can have abstractable hydrogens. The reaction may also be conducted in the presence of synthetic ester lubricants produced from condensation of monohydroxy alcohols and/or polyhydroxy alcohols with monocarboxylic or polycarboxylic acids as described above. Other useful solvents for the reaction of DPA, PANA, and organic peroxides are the alkane solvents having from 6 to 16 carbons atoms in a linear, branched, or cyclic structure. These solvents are easily removed by volatilization.

Subsequent to the reaction of the DPA, PANA, and organic peroxides, it is desirable to raise the temperature of the reaction mixture to fully decompose the organic peroxides. Under optimized conditions as recited above, most of the desired reactions which form homo-oligomers and cross oligomers have occurred prior to the residual peroxide decomposition step. The peroxide decomposition step is conducted at temperatures in the range of about 140°C to about 200°C for a time period in the range of about 5 minutes to about 2 hours and preferably at pressures below atmospheric pressure.

Reaction in accordance with the above-described conditions results in greater than 70 mole % of the DPA and PANA being in oligomeric forms of dimer or higher. Any residual portion of the DPA and PANA is predominantly in monomer form and is present with the DPA and PANA that are also part the three component additive.

Any organic peroxide which has a half life of about one hour at temperatures in the range of about 70°C to about 200°C may be used as a free radical source. Included in this group are acyl peroxide, peresters, peroxyketals, and alkyl peroxides, all of which are commercially available. The amount of peroxide used is typically in the range of about 0.5 to 3.0 moles/mole of diaryl amines.

A thorough discussion and further characterization of these oligomers may be found in EPO Patent No. EP 734 432 B.

The preferred concentration of this oligomer component is from about 0.2 to about 5.0 percent by weight of the fully formulated lubricating oil composition.

Oligomer Preparation

DODPA (783 g, 2 mole), Irganox LO-6®, (331.5 g 1 mole), and 1114.5 g of technical pentaerythritol ester were placed in a 5-liter 3-neck flask equipped with a thermometer, an addition funnel and a distillation column. Irganox LO-6® is an octylated PANA having a molecular formula of $C_{24}H_{29}N$ and wherein the octyl group is highly branched (1,1,3,3-tetramethylbutane). Irganox LO-6® is available from CIBA-GEIGY. The reaction mixture was heated to 140°C under nitrogen. Di-t-butyl peroxide (526.3 g, 3.6 mole) was added in portions over 45 minutes. The reaction was continued for 3 hours during which time t-butyl alcohol was collected through the distillation column with a head temperature of 80-85°C. The color went from a fluorescent bluish color to a brown color. The reaction temperature was then raised to 170°C over a 1-hour period and was maintained at 170°C for 40 minutes. More t-butyl alcohol was collected. A vacuum was then slowly applied to accelerate the distillation until a pressure of 2 mm of Hg was reacted. The reaction mixture was held under those conditions for 20 minutes to remove all residue alcohol. The vacuum was released under nitrogen and the mixture was cooled down. The reaction product was then collected as a 50 % by weight active ingredient in the lubricant.

Examples 1-4

For Examples 1-4, the base turbine oil formulation used in all instances was a technical grade pentaerythritol ester further containing tricresyl phosphate antiwear additive, toluotriazole and sebacic acid corrosion inhibitors and thiodipropionic acid and amine phosphate load additives. The DPA component deployed in Examples 1, 2, and 4, was dioctyl-diphenyl amine (DODPA). The PANA component deployed in Examples 1, 2 and 3, was Irganox LO-6® which is an octylated PANA having a molecular formula of $C_{24}H_{29}N$ and wherein the octyl group is highly branched (e.g., 1,1,3,3-tetramethylbutyl). Irganox LO-6® is available from CIBA-GEIGY. The oligomer component, deployed in Examples 1, 3 and 4, was prepared as disclosed above.

For Example 1, all three components were added to the base oil so as to make up a total of 3.0 weight percent of the fully formulated lubricating oil composition. For Example 2, only the DPA and PANA components were added to the base oil so as to make up a total of 3.0 weight percent of the fully formulated lubricating oil composition. For Example 3, only the oligomer and PANA components were added to the base oil so as to make up a total of 3.0 weight percent of the fully formulated lubricating oil composition. For Example 4, only the oligomer and DPA components were added to the base oil so as to make up a total of 3.0 weight percent of the fully formulated lubricating oil composition. Thus for Examples 1-4, the total amount of aryl amine additives remained constant at 3.0 weight percent of the fully formulated lubricating oil composition.

The formulations of Examples 1-4 were submitted to the Alcor High Temperature test. The Alcor High Temperature test is a standard deposition test run for synthetic engine oils and is part of the General Electric Specification D50TF1. The test can be run at temperatures from 525 to 600°F (274 to 316°C). The tests on Examples 1-4 were run at 550°F (288°C). In the test, oil passes from a reservoir through a filter and pump to a coking unit. The oil

enters the coking section at 300°F (149°C) and is exposed to a resistance-heated tube where the oil encounters a temperature gradient from 550°F (288°C) in the lower tube section up to approximately 700°F (371°C). After a 48-hour period, the apparatus is disassembled, the tube deposit is weighed and rated and used (tested) oil viscosity and total acid number (TAN) measured. The results obtained for Examples 1-4 are summarized in Table 1 below.

Table 1

Example Number	1(a)	1(b)	2	3	4
Oligomer Component (wt %)	1.4	1.4	--	1.4	1.4
DPA Component (wt %)	1.1	1.1	1.7	--	1.6
PANA Component (wt %)	0.5	0.5	1.3	1.6	--
Total 3 Component (wt %)	3.0	3.0	3.0	3.0	3.0
Alcor Test Deposit Wt. (g)	7	6	10	9	5
Alcor Test Deposit Rating	1	1	7	5.5	1.8
Alcor Test Delta Vis	15.7	13.4	26.6	22.1	22.1
Alco Test Delta TAN	0	-0.2	0	-0.12	0.35

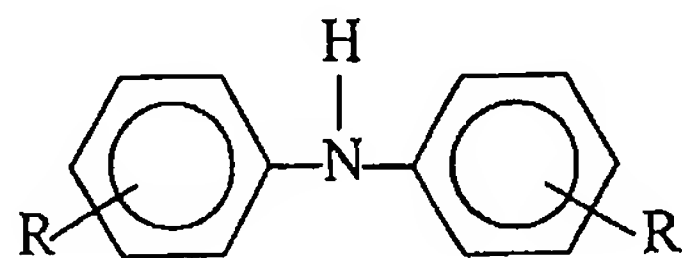
Examples 1(a) and 1(b), which are mixtures of all three antioxidant components, provide the best overall test performance. Examples 2 and 3 did not provide the same low level of deposit performance or viscosity increase control. Example 4 gave a slightly lower tube deposit weight, but directionally poorer rating and did not provide the same level of viscosity and TAN control as these data, that a synergistic combination of an oligomer component, a DPA component, and a PANA component provides better thermal and oxidative stability than two component combinations of oligomer/DPA, oligomer/PANA, or DPA/PANA.



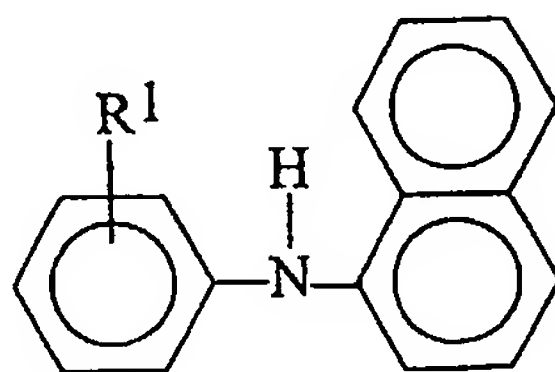
Reasonable variation and modification are possible in the scope of the foregoing disclosure and the appended claims to this invention, the essence of which is that a three component aryl amine antioxidant turbine oil additive provides superior performance over all possible permutations of two component
5 aryl amine antioxidant turbine oil additives.

Claims

1. A turbine oil composition exhibiting enhanced resistance to deposition and improved oxidative stability, said turbine oil formulation comprising a major portion of a synthetic ester based base stock and a minor portion of an additive package comprising a DPA component as given by



where R is an alkyl group having from about 4 to about 12 carbon atoms; a PANA component as given by



- 10 where R^1 is selected from the group consisting of H, an alkyl group containing from about 4 to 12 carbon atoms, and an alkaryl group containing from 7 to 12 carbon atoms; and an oligomer formed by the reaction of a DPA component and a PANA component in the presence of at least one organic peroxide at an elevated temperature.
- 15 2. The composition of claim 1 wherein the synthetic ester based stock is the esterification product of an aliphatic polyol containing 4 to 15 carbon atoms



and from 2 to 8 esterifiable hydroxyl groups reacted with a carboxylic acid containing from 4 to 12 carbon atoms.

3. The composition of claim 1 wherein the synthetic ester stock is the esterification product of technical pentaerythritol and a mixture of C₄ to C₁₂ carboxylic acids.

4. The turbine oil composition of any one of the preceding claims wherein the total weight of the DPA, PANA, and oligomer additives comprises from about 0.5 to about 10 weight percent of the fully formulated lubricating oil composition.

10 5. The turbine oil composition of any one of the preceding claims wherein the DPA component comprises from about 0.2 to about 5 weight percent of the fully formulated lubricating oil composition.

6. The turbine oil composition of any one of the preceding claims wherein the PANA component comprises from about 0.2 to about 5 weight percent of the fully formulated lubricating oil composition.

7. The turbine oil composition of any one of the preceding claims wherein the oligomer component comprises from about 0.2 to about 5 weight percent of the fully formulated lubricating oil composition.

8. The turbine oil composition of any one of the preceding claims wherein the DPA component comprises a dioctyl-diphenyl amine.

9. The turbine oil composition of any one of the preceding claims wherein R¹ is a branched alkyl group having 8 carbon atoms.

10. The turbine oil composition of claim 9 wherein R¹ is 1,1,3,3-tetramethylbutyl.

25 11. The turbine oil composition of any one of the preceding claims wherein the oligomer component is formed by the reaction of a dioctyl-diphenyl amine and an octylated PANA in the presence of at least one organic peroxide at an elevated temperature.

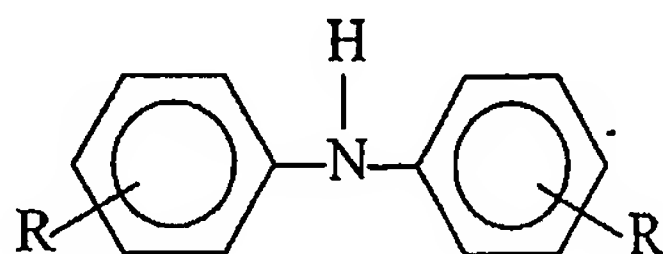
12. The turbine oil composition of any one of the preceding claims wherein the oligomer forming reaction comprises the use of a molar ratio of DPA:PANA in the range of about 1:1 to about 10:1.

13. The turbine oil composition of any one of the preceding claims wherein the oligomer forming reaction comprises the use of a molar ratio of DPA:PANA in the range of about 1.2:1 to about 5:1.

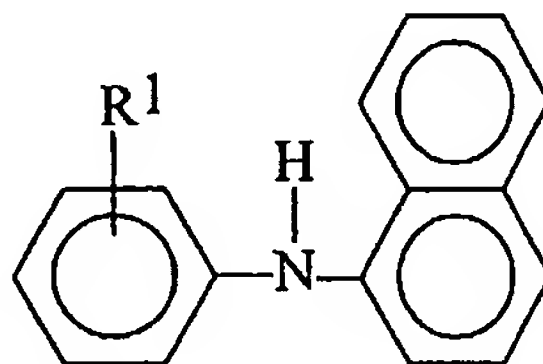
14. The turbine oil composition of any one of the preceding claims wherein the organic peroxide comprises di-t-butyl peroxide.

15. The turbine oil composition of any one of the preceding claims wherein the elevated reaction temperature is in the range of about 70°C to 200°C.

16. A method for enhancing the resistance to deposition and improving the oxidation stability of a synthetic ester based stock by adding to said turbine oil an additive comprising a DPA component as given by



where R is an alkyl group having from about 4 to about 12 carbon atoms; a PANA component as given by



where R¹ is selected from the group consisting of H, an alkyl group containing from about 4 to 12 carbon atoms, and an alkaryl group containing from 7 to 12 carbon atoms; and an oligomer formed by the reaction of a DPA component

and a PANA component in the presence of at least one organic peroxide at an elevated temperature.

17. The method of claim 16 wherein the synthetic ester based stock is the esterification product of an aliphatic polyol containing 4 to 15 carbon atoms and from 2 to 8 esterifiable hydroxyl groups reacted with a carboxylic acid containing from 4 to 12 carbon atoms.

18. The method of claim 16 wherein the synthetic ester based stock is the esterification product of technical pentaerythritol and a mixture of C₄ to C₁₂ carboxylic acids.

19. The method of any one of claims 16 to 18 wherein the total weight of the DPA, PANA, and oligomer additives comprises from about 0.5 to about 10 weight percent of the fully formulated lubricating oil composition.

20. A turbine oil composition as claimed in claim 1, substantially as herein described.

21. A method for enhancing the resistance to deposition and improving the oxidation stability of a synthetic ester based stock as claimed in claim 16, substantially as herein described.



Application No: GB 0222911.0
Claims searched: 1-21

Examiner: Fiona Warner
Date of search: 15 May 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-3 & 16-18 at least	GB 1059489 A (TENNECO) see in particular page 1, line 7 to page 2, line 58
A		US 3665038 A (MOBIL)
X	1, 16 at least	WPI Abstract Accession No. 1997-539607 [50] & JP 9217078 A (TONEN) 19.08.1997
X	1, 16 at least	WPI Abstract Accession No. 1995-332762 [43] & JP 7228882 A (COSMO) 29.08.1995
X	1, 16 at least	WPI Abstract Accession No. 1992-295560 [36] & JP 4202398 A (TONEN) 23.07.1992

Categories:

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^v:

C5E; C5F

Worldwide search of patent documents classified in the following areas of the IPC⁷:

C07C; C10M

The following online and other databases have been used in the preparation of this search report :

Online (EPODOC, WPI, PAJ)